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<p>(54) Title: FIRE-RESISTANT GAS GENERATING BATTERY ELECTROLYTES</p> $  \begin{array}{c}  A_n - X - B^1_n \\    \\  B^2_n  \end{array}  \quad (I)  $ <p>(57) Abstract</p> <p>A compound that generates a fire-retardant gas upon decomposition has general structure (I) wherein, X is N, C, S, NO, N<sub>2</sub>, CO, SO; A is substantially any organic moiety including alkyl, aryl, alkoxy, cyclic, fused cyclic, heteroatoms, ketals, acetals or alcohols. B<sup>1</sup> and B<sup>2</sup> are substantially any organic moiety including alkyl, aryl, alkoxy, cyclic, fused cyclic, heteroatoms, ketals, acetals or alcohols, also including oxygen, hydrogen and null; and n is an integer from 0-100. Preferred gases generated thereby include CO, SO<sub>2</sub>, SO<sub>3</sub>, NO, N<sub>2</sub>O, NO<sub>2</sub> and N<sub>2</sub>. It is also preferred that the generated gas assists in formation of a solid electrolyte interface (SEI) between the electrolyte and at least one of the electrodes. It is most preferred that the cell have a conductivity greater than 10<sup>-3</sup> S/cm.</p>		

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## FIRE-RESISTANT GAS GENERATING BATTERY ELECTROLYTES

### Field of The Invention

The field of the invention is batteries, and especially battery electrolytes.

### 5 Background

Battery power is considered one of the more convenient and better performing choices as a power supply in many applications, including portable and backup applications.

Advantages to utilizing battery power include portability, isolation from power lines and from earth ground, minimization of heat management, and uninterruptibility in light of  
10 momentary ac power interruptions.

Batteries find application in back-up power, electric and hybrid vehicles, and consumer electronics. Exemplary applications include lightweight hand-held instruments, such as data loggers that make measurements in difficult environments including the ocean floor or high altitudes, and larger stand-alone instrumentation, such as backup power  
15 sources for telephone lines. Smaller primary and rechargeable batteries can have many applications in consumer electronics such as video cameras, cellular telephones, personal data assistants, mini-disks and computers. Larger batteries can have applications in back-up power and vehicles. However, as the size of the battery increases, the potential hazards of operation substantially increase.

20 Batteries comprise two major components: (1) electrodes, specifically an anode and a cathode, and (2) an electrolyte. The electrode is a phase through which charge is carried by electronic movement. Electrodes can be metals or semiconductors, and they can be solid or liquid. The electrolyte is generally defined as a phase through which charge is carried by the movement of ions. Electrolytes may be any phase on the continuum of liquid to solid,  
25 including gels, pastes, fused salts, or ionically conducting solids, such as sodium  $\beta$ -alumina, which has mobile sodium ions. (Bard, Allen J. and Larry R. Faulkner, Electrochemical Methods: Fundamentals and Applications, John Wiley & Sons (New York), 1980).

The electrolyte is generally the most unstable component of a battery or cell, particularly because it can be compromised or decomposed much faster than the electrodes.

When the electrolyte is subject to decomposition, an explosive release of energy and reactive materials can result. A hazard is created for both the operator and the device that is being powered by the cell. Highly exothermic reactions have been known to occur when primary lithium batteries are subjected to temperatures above the recommended levels, or  
5 when rechargeable cells are subjected to unusual or severe conditions of discharging or recharging. (Ebner et al., *Proc. 30<sup>th</sup> Power Sources Symp.*, p.119, (1982)). For example, primary lithium cells using a lithium thionylchloride system have been known to undergo highly exothermic reactions when subjected to temperatures above or below the recommended temperatures. In the case of secondary cells, subjecting the cells to unusual  
10 or severe recharging conditions, and deposition of lithium in a highly porous film on the anode have led to similar disastrous results. (Pasquariello et al., *Proc. Symp. Lithium Batteries*, 93-24: 106, (1993)).

In an attempt to circumvent some of the above-mentioned hazards with electrolytes, electrolytic materials have been developed that are initially fire-resistant. This means that  
15 the composition of the electrolyte is fire-resistant when that composition is initially produced.

US 5,455,127 issued to Olsen et al. (October 1995) discusses the addition of a flame retardant directly to the electrolyte, such as trimethyl phosphate or trimethylene phosphate. In other words, it is known as a general principle that the flame retardant chemical can be  
20 physically incorporated into the original electrolyte. In embodiments incorporating that principle, the electrolytic composition can remain fire retardant, as long as the original electrolyte and the fire retardant additive remain chemically intact with respect to one another.

US 5,580,684 issued to Yokoyama et al. (December 1996) also discusses the  
25 addition of a flame retardant directly to the electrolyte similar to the additives discussed in Olsen et al. Yokoyama '684 differs from Olsen '127, however, in that Yokoyama '684 discusses the addition of carbonates to the electrolyte along with the addition of phosphoric acid esters to increase the inflammation point of the electrolyte. The carbonate additives are quite stable within the electrolyte composition, and are designed to remain stable within the  
30 electrolyte. This carbonate stability is considered to be constant regardless of the physical

state of the electrolyte. The carbonate additives chosen by Yokoyama are so stable that when the electrolytic composition decomposes, the carbonate additives do not release carbon dioxide as a byproduct of the decomposition.

5        There are many disadvantages to electrolytic compositions described above by Olsen and Yokoyama. For example, once the electrolytic composition begins decomposing, the fire-resistant properties decrease and subsequently become ineffective. Therefore, an electrolytic composition that would retain its fire-resistant properties or possibly develop fire-retardant properties upon decomposition would be an improvement over the compositions suggested by Olsen or Yokoyama.

10        US 5,830,600 issued to Narang et al. (November 1998) teaches electrolytic compositions comprising a lithium salt mixed with classes of liquid electrolyte solvents. The resulting electrolytic composition comprises a dicarbonate, ester, perester, dioxalate, acyl peroxide, peroxodicarbonate, or Diels-Alder adduct of carbon dioxide, or mixtures thereof. This electrolytic composition is not only designed to be initially fire-resistant, but  
15        additionally is designed to become fire-retardant upon decomposition of the electrolyte. In other words, when the electrolyte decomposes, carbon dioxide gas is generated that retards ignition of the electrolytic material and extinguishes any subsequent fire caused by the decomposition of the electrolytic material.

20        Narang et al., however, describe carbon dioxide as the only decomposition gas generated. Electrolytes produced from chemicals that generate carbon dioxide upon decomposition have some drawbacks, with respect to particular applications, and may adversely affect the overall performance of certain battery cells.

25        Therefore, there is still a need to provide electrolytic compositions that are fire-retardant upon decomposition, and especially compositions that are capable of producing fire-retarding gases other than carbon dioxide.

**Summary of the Invention**

The present invention is directed to an improvement over a conventional battery having at least two electrodes and an electrolyte, in which a compound according to **Structure I** is added to the electrolyte to generate a fire-retardant gas upon decomposition  
 5 of the electrolyte. Preferred gases are CO, SO<sub>2</sub>, SO<sub>3</sub>, NO, N<sub>2</sub>O, NO<sub>2</sub>, and N<sub>2</sub>.

**Structure I** has the following formula:



**Structure I**

15 wherein,

X = N, C, S, NO, N<sub>2</sub>, CO, SO;

20 A = aryl (including conjugated, non-conjugated), alkyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkenyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkoxy (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted),  
 25 aralkylene (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), annulene (i.e. completely conjugated monocyclic polyenes), conjugated hydrocarbons (such as fulvene, calicene, fulvalene, methylenecyclopropene), fused ring systems (such as naphthalene, anthracene, naphthacene, phenanthrene, triphenylene, pyrene, perylene, butalene, pentalene,  
 30 azulene, heptalene, biphenylene, acenaphthylene), heteroatoms (including halogen, alkali metals, transition metals), alcohol (such as phenol, ethanol, butanol), hydroxyl, acetal, or ketal;

35 B<sup>1</sup> and B<sup>2</sup> = null, oxygen, hydrogen, aryl (including conjugated, non-conjugated), alkyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkenyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkoxy (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), aralkylene (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted),  
 40 annulene (i.e. completely conjugated monocyclic polyenes), conjugated hydrocarbons (such as fulvene, calicene, fulvalene, methylenecyclopropene), fused ring systems (such as naphthalene,

anthracene, naphthacene, phenanthrene, triphenylene, pyrene,  
perylene, butalene, pentalene, azulene, heptalene, biphenylene,  
acenaphthylene), heteroatoms (including halogen, alkali metals,  
transition metals), alcohol (such as phenol, ethanol, butanol),  
hydroxyl, acetal, or ketal;

n = an integer from 0-100;

where B<sup>1</sup> and B<sup>2</sup> are not null simultaneously;

where B<sup>2</sup> is null when X is N<sub>2</sub>; and

where B<sup>1</sup> and B<sup>2</sup> are not oxygen when X is CO.

In one aspect of preferred embodiments, a solid electrolyte interface (SEI) is formed on the anode material at least in part using a substantially compatible (i.e., SEI developing) electrolyte.

Various objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the invention, along with the accompanying drawings in which like numerals represent like components.

### Detailed Description

The practice of the present invention can employ, unless otherwise indicated, conventional techniques of battery fabrication, battery chemistry, and electrolyte chemistry. All patents, patent applications, publications and other types of references cited herein, whether supra or infra, are hereby incorporated by reference in their entirety. Despite the incorporation of references, the present text does not necessarily adopt the definitions and usages set forth in the references. Therefore, to clarify the definitions and usages of specific terms that are not defined elsewhere herein, we set forth the following.

The singular forms "a", "an" and "the" are used herein to include the plural unless the content clearly dictates otherwise. Thus, for example, reference to "an electrolyte additive" includes mixtures of such additives, reference to "the anode material" includes more than one such material, and the like.

As used herein the term "electrode" is used herein to mean a phase through which charge is carried by electronic movement. Electrodes can be metals or semiconductors, and they can be solid or liquid. Also as used herein, the term "electrolyte" is generally defined as a phase through which charge is carried by the movement of ions. Electrolytes may be  
5 any phase on the continuum of liquid to solid, including gels, pastes, fused salts, or ionically conducting solids, such as sodium  $\beta$ -alumina, which has mobile sodium ions.

The phrases "electrolyte additive" and "compound that generates a fire-retardant gas upon decomposition" are used interchangeably herein to mean a substance that could be added to a base electrolyte in measured concentrations for a definite purpose. Electrolyte  
10 additives may be divided into two groups: 1) Those which have an auxiliary or secondary function, such as thickeners, plasticizers, flame-retardants, colorants, etc., and 2) Those that are essential to the existence of the end product, which is the electrolyte. The second classification of electrolyte additives should be regarded less as additives than as base materials, since the electrolyte could not exist without them. In other words, some  
15 electrolyte additives may inherently act as the electrolyte itself in a cell or at the very least be an important base in the final electrolytic composition.

As used herein the terms "anode material" and "anode" are used interchangeably, except where the context clearly indicates otherwise. Similarly, the terms the terms  
"cathode material" and "cathode" are used interchangeably. These definitions are intended  
20 to eliminate confusion over the exact point at which the respective electrode material(s) is/are incorporated into, and thus becomes an electrode.

The term "metal" is used herein broadly to mean a composition having metallic properties, such as metallic luster, electrical conductivity, high chemical reactivity, and substantial physical strength. The definition includes an element selected from one of the  
25 metal and transition metal groups of the periodic table, alloys of such metals, metal ceramics (inclusions), superalloys, fusible alloys, and amalgams.

The terms "fire-retardant", "flame-retardant", "fire-resistant" and "nonflammable" are used interchangeably herein to mean a reduction or elimination of the tendency of a combustible material to burn, i.e., a "fire-retardant" material is one having a lower ignition  
30 susceptibility or, once ignited, lower flammability. Thus, a "fire-retardant electrolyte

- composition" is one in which the basic flammability has been reduced as measured by accelerated rate calorimetry (*see, e.g. Von Slacken et al. Proc. Seventh Int'l Meeting on Lithium Batteries*, p. 12 (1994)), or by one of the art-accepted standard flame or heat impingement tests, or other standard test of reduced flammability, for example, ASTM
- 5 D2863 (limiting oxygen index) (*see, e.g., Tests for Flammability of Plastic Materials for Parts in Devices and Appliances*, Underwriters Laboratories, Northbrook, IL, 1991; *National Fire Codes*, National Fire Protection Association, Quincy, MA, 1992; *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products*, American Society for Testing and Material, Philadelphia, PA, 1991; *see, also, "Fire*
- 10 *Retardants"* in *Encyclopedia of Polymer Science and Engineering*, Second Edition, Vol. 10, pp.930-1022, John Wiley & Sons (New York), 1988).

- The term "alkyl" is used herein to mean a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like.
- 15 Preferred alkyl groups herein contain 1 to 12 carbon atoms.

The term "alkenyl" is used herein to mean a branched or unbranched hydrocarbon chain containing from 2 to 24 carbon atoms and at least one double bond. Preferred alkenyl groups herein contain 1 to 12 carbon atoms.

- The term "alkoxy" is used herein to mean an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group may be defined as -OR wherein R is alkyl as defined above.
- 20

- The term "aryl" is used herein to mean a monocyclic aromatic species of 5 to 7 carbon atoms, and is typically phenyl. Optionally, these groups are substituted with one to four, more preferably one to two, lower alkyl, lower alkoxy, hydroxy, and/or nitro
- 25 substituents.

The term "aralkylene" is used herein to mean moieties containing both alkylene and monocyclic aryl species, typically containing less than about 12 carbon atoms in the alkylene portion, and wherein the aryl substituent is bonded to the structure of interest

through an alkylene linking group. Exemplary aralkylene groups have the structure  $-(CH_2)_j-$  Ar wherein "j" is an integer in the range of 1 to 6 and wherein "Ar" is an aryl species.

The terms "halogen" and "halo" are used to mean fluoro, chloro, bromo, or iodo, and usually relates to halo substitution for a hydrogen atom in an organic compound.

5 A "lithium ion-conducting compound" is used herein to mean a composition capable of transporting lithium ions with sufficient low resistivity to be useful in a battery electrolyte. Lithium ion-conducting compounds include single-ion conducting polymer electrolytes as described in commonly assigned US Patent No. 5,061,581 issued to Narang et al., as well as in US Patent No. 5,548,055, entitled "Single-Ion Conducting Solid Polymer  
10 Electrolytes", issued to Narang et al. (August 1996). The disclosures of both of the aforementioned documents are incorporated herein by reference. Thus, a flame-retardant electrolyte composition may be prepared by dissolving a single-ion conducting polymer electrolyte in one of the electrolyte additives described herein. Preferred lithium ion-conducting compounds include compounds of the formula Li-A, wherein A is an anion  
15 which may be Cl, CF<sub>3</sub>SO<sub>3</sub>, ClO<sub>4</sub>, BF<sub>4</sub>, Br, I, SCN, AsF<sub>6</sub>, N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, PF<sub>6</sub>, SbF<sub>6</sub>, O(CO)R<sup>1</sup>, wherein R<sup>1</sup> is H, alkyl, aryl, alkenyl, halo, or the like. Preferred ion-conducting compounds include, for example, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, and mixtures thereof. Solutions of lithium ion-conducting compounds in fire-retardant additives are preferably prepared to achieve 0.2 M to 2.0 M lithium, most preferably 0.5 M to 1.5 M lithium.

20 "Optional" or "optionally" means that the subsequently described circumstance may or may not occur, and that the description includes instances in which said circumstance occurs and instances in which it does not. For example, the phrase "Optionally, these groups are substituted..." means that these groups may or may not be substituted and that the description includes both the instance when the groups are substituted and the instance  
25 when the groups are not substituted.

Also as used herein, the term "effective SEI" means an interface between an anode and an electrolyte in a metal ion cell that is sufficiently impermeable to the electrolyte and solvent, and sufficiently permeable to the transit of the relevant ions, to provide a cycle life of at least 50 cycles.

The term "compatible" is employed herein to mean the ability of a given electrolyte to form an effective SEI on a particular anode material of interest. Substantially compatible electrolytes with respect to a particular anode material are those which tend to form an effective SEI on that material, while substantially incompatible electrolytes are those which generally fail to form an effective SEI on the anode material and undergo decomposition on the electrode. Where an electrolyte composition contains many electrolyte species, including perhaps multiple solvents, the electrolyte composition is taken as a whole when determining whether the electrolyte composition is substantially compatible or substantially incompatible. There are, of course, boundary conditions in which an electrolyte forms an effective SEI with a given anode material either very slowly, or only under special conditions. In such boundary conditions, the electrolyte is deemed to be substantially incompatible with the anode material. It should also be understood that the term "compatible" is specific to particular anode materials. Propylene carbonate, for example, is substantially compatible with coke anodes, but substantially incompatible with graphite anodes.

To avoid possible confusion between a single cell and a battery which may have one or more cells, the terms "cell" and "battery" are used interchangeably, except where the context clearly indicates otherwise.

## Cell Chemistries

The particular overall chemistry involved in contemplated batteries is not critical, although it is contemplated that battery chemistries yielding higher voltages will generally derive greater benefit. For this and other reasons, lithium ion chemistries are generally considered among the metal ion batteries to have the greatest commercial utility and applicability for the present invention, and the following discussion focuses primarily on lithium ion batteries. Nevertheless, it should be understood that appropriate correspondences should be extrapolated to other types of metal ion batteries.

### Electrolyte Composition

An electrolyte may occur in any form, including liquid, semi-solid, or even solid. Of course, the electrolyte must cooperate with the active electrode material(s) to provide chemical reactions that store and release electrical energy, and many such chemistries are already known. Thus, for lithium ion batteries, the electrolyte is generally selected from a lithium ion-conducting chemical such as lithium hexafluorophosphate in ethylene carbonate and dimethyl carbonate, or a mixture of ethylene carbonate/dimethyl carbonate/triethylphosphate. Also, for safe operation of the cell, the electrolyte may advantageously be chosen from a non-flammable group of chemicals.

The electrolyte may be stable or unstable on the electrode. Many known electrolytes having desirable characteristics such as low volatility, high flash point, low freezing point, or high dielectric constant, for example, are unstable on the electrodes and will ultimately affect the formation of the solid electrolyte interface (SEI).

The electrolyte may comprise polymeric materials that are molecularly arranged as linear, branched, cross-linked, cycloliner, ladder, cyclomatrix, copolymer, terpolymer, or graft copolymer. Electrolytes may further comprise polymeric materials that can be defined with respect to phase as a thermoplastic, an elastomer, a plasticizer, a thermosetting resin or a polymer blend.

Several of the polymer electrolytes mentioned above could be considered for use in high temperature conditions, such as those commonly experienced in batteries or cells. Examples of high temperature perfluorinated polymer electrolytes include perfluorosulfo poly(p-phenylenes), perfluorosulfo poly(p-phenyleneoxide), perfluorosulfo poly(p-phenylenesulfide), perfluorosulfo poly(p-phenylenesulfones), perfluorosulfo aromatic polyamides, perfluorosulfo aromatic polycarbonates, perfluorosulfo polyimides, perfluorosulfo polybenzazoles, perfluorosulfo poly(quinoxalines), perfluorosulfo poly(quinolines), and other perfluorosulfo high temperature polymers whose corresponding non-fluorinated non-sulfonated analogs are described by C. Arnold in Journal of Polymer Science: Macromolecular Reviews, vol.14, pp. 265-378 (1979), K. Hodd in Trends in Polymer Science, vol.1 no.5, pp. 129-137 (May 1993), Chyi-Shan Wang in Trends in Polymer Science, vol.1, no.7, pp. 199-205 (July 1993), and references therein, and in

Advances in Polymer Science, vol. 117 "High Performance Polymers", Springer-Verlag (1994).

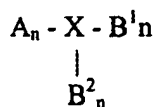
- High temperature polymer electrolytes can also be formulated from blends, interpenetrating or semi-interpenetrating networks containing the described polymers, or by preparing composites of the described polymers with ceramics, such as alumina or silica. Examples of other combinations are set forth in Table 1.

TABLE 1

<u>Chemistry</u>	<u>Electrolyte</u>	<u>Anode Material</u>	<u>Cathode Material</u>	<u>Peak Sustained Power (W/Kg)</u>	<u>Total Energy To Full Discharge (Wh/Kg)</u>
Lead Acid	sulfuric acid	Pb	PbO <sub>2</sub>	300-400	35-50
Lithium ion	organic	Carbon	LiM <sub>x</sub> O <sub>y</sub>	200-250	100-125
NiCd	alkaline	NiOOH	Cd	350-450	40-50
Li/TiS <sub>2</sub>	organic	Li	TiS <sub>2</sub>	150-175	90-110
NiMH	alkaline	NiOOH	Metal alloys	200-300	80-90

### Electrolyte Additive

Structure 1 shows the generic structure for a compound that can be added to an electrolyte to form an improved battery.



Structure I

wherein,

X = N, C, S, NO, N<sub>2</sub>, CO, SO;

5 A = aryl (including conjugated, non-conjugated), alkyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkenyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkoxy (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), aralkylene (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), annulene (i.e. completely conjugated monocyclic polyenes), conjugated hydrocarbons (such as fulvene, calicene, fulvalene, methylenecyclopropene), fused ring systems (such as naphthalene, anthracene, naphthacene, phenanthrene, triphenylene, pyrene, perylene, butalene, pentalene, azulene, heptalene, biphenylene, acenaphthylene), heteroatoms (including halogen, alkali metals, transition metals), alcohol (such as phenol, ethanol, butanol), hydroxyl, acetal, or ketal;

10 B<sup>1</sup> and B<sup>2</sup> = null, oxygen, hydrogen, aryl (including conjugated, non-conjugated), alkyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkenyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkoxy (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), aralkylene (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), annulene (i.e. completely conjugated monocyclic polyenes), conjugated hydrocarbons (such as fulvene, calicene, fulvalene, methylenecyclopropene), fused ring systems (such as naphthalene, anthracene, naphthacene, phenanthrene, triphenylene, pyrene, perylene, butalene, pentalene, azulene, heptalene, biphenylene, acenaphthylene), heteroatoms (including halogen, alkali metals, transition metals), alcohol (such as phenol, ethanol, butanol), hydroxyl, acetal, or ketal;

15 n = an integer from 0-100;

35 where B<sup>1</sup> and B<sup>2</sup> are not null simultaneously;

where B<sup>2</sup> is null when X is N<sub>2</sub>; and

where B<sup>1</sup> and B<sup>2</sup> are not oxygen when X is CO.

Structure I can be synthesized using standard organic synthesis methods described in the chemical literature, such as those reactions found in Advanced Organic Chemistry  
 40 Third Edition; Part A: Structure and Mechanisms and Part B: Reactions and Synthesis.  
 Francis A. Carey and Richard J. Sundberg, Plenum Press (New York), 1990.

Several of the most common and most appropriate organic reactions that may be employed to synthesize **Structure I** include the following classes of reactions: Alkylation of a Nucleophilic Carbon (including Alkylation of enolates, dianions, aldehydes, esters, amides, and nitriles, and Alkylation of carbon nucleophiles by conjugate addition); and  
5 reactions of carbon nucleophiles with carbonyl groups (including the Aldol condensation, Mixed Aldol condensations, Intramolecular Aldol condensations, Condensation reactions of Imines and Iminium Ions, the Mannich Reaction, Amine-Catalyzed Condensation reactions, the Wittig Reaction, and Nucleophilic Addition - Cyclization).

Further, other common organic reactions that are appropriate for forming **Structure I** are: Functional Group Interconversion by Nucleophilic Substitution (including the  
10 conversion of alcohols to alkylating agents, introduction of functional groups by nucleophilic substitution at saturated carbon, nucleophilic cleavage of carbon-oxygen bonds in ethers and esters, interconversion of carboxylic acid derivatives); Electrophilic additions to carbon-carbon multiple bonds (including hydration, addition of hydrogen halides, and  
15 hydroboration); Reduction of Carbonyl and other Functional Groups (including Catalytic Hydrogenation, reduction by hydride donors, dissolving-metal reductions); Cycloadditions (including the Diels-Alder Reaction, Dipolar Cycloaddition Reactions, Photochemical Cycloaddition Reactions); Unimolecular Rearrangements (including the Cope and Claisen Rearrangements and other Sigmatropic Rearrangements); and Thermal Elimination  
20 Reactions (including Cheletropic Elimination, Decomposition of Cyclic Azo Compounds, and  $\beta$ -Eliminations).

Still further, appropriate organic syntheses that can be used for the formation of **Structure I** are as follows: Reactions of Organometallic Compounds; Reactions Involving Transition Metals; Reactions Involving Highly Reactive Electron-Deficient Intermediates  
25 (including Carbenes, Nitrenes, Free-Radical Intermediates, and Carbocations); Aromatic Substitution Reactions (including Electrophilic Aromatic Substitution, Friedel-Crafts Alkylations and Acylations, Nucleophilic Aromatic Substitution, Aromatic Radical Substitution, and Substitution by the  $S_{RN}1$  Mechanism); Oxidation Reactions (including ozonolysis, selective oxidative cleavages, and allylic oxidation) and Multistep Syntheses  
30 (including using protective groups, and the control of stereochemistry).

Table 2 shows 34 representative examples of compounds that can be employed as electrolyte additives. Compounds 1-9 can be considered preferable compounds to incorporate as electrolyte additives because they are commercially available. Compounds 10-34 can be considered as examples of other possible electrolyte additives that may or may not be commercially available at this time.

### Electrodes

An electrode, such as an anode or a cathode, may occur in any form, including solid, semi-solid, or even liquid. Of course, the electrode must cooperate with the electrolytic material(s) to provide chemical reactions that store and release electrical energy, and many such chemistries are already known. Electrodes can be made from a number of materials, including but not limited to lead, lead dioxide, zinc, lithium, aluminum, copper, iron, manganese dioxide, nickel, cadmium, mercury, titanium, and graphite.

For lithium ion batteries, the anode is preferably fabricated using a material capable of intercalating lithium. Various metal oxides and chalcogenides satisfy this requirement, including especially tin oxide, molybdenum oxide, tungsten oxide, and titanium disulfide. Any suitable form of carbon may alternatively be used for the anode, include coke, synthetic or natural graphite, mesophase microbeads, a soft or hard disordered carbon, and the like. Combinations of anode materials are also contemplated. It is particularly contemplated, however, that the anode material comprises at least 15%, 25%, 50%, 75% or 90% of a compound selected from the group comprising at least one metal oxide, at least one chalcogenide, and at least one form of carbon.

The anode material may advantageously be supported by a current collector. Nickel, copper, stainless steel, and titanium are all suitable current collectors. The anode material may also be bound to the support by a suitable binder, such as fluororesin, polyvinylidene fluoride, ethylene-propylene-diene copolymer, styrene-butadiene rubber, carboxymethylcellulose, and the like. Such binders may be present in any appropriate amount from about 1% to about 20% by weight of the active electrode material, and more preferably from about 5% to about 10% by weight. A conducting filler may also be present with the binder, such as acetylene black or graphite in an amount of from about 1% to about

20% of the weight of the binder and active electrode material and preferably from about 2% to about 5%.

The cathode material is preferably a lithiated metal oxide. Any lithiated metal oxide may be used for this purpose, such as one or more of lithiated nickel oxide, manganese  
5 dioxide, or cobalt oxide. The lithiated metal oxide may also be affixed to a support using a suitable binder. Known supports for this purpose are aluminum, aluminum alloys, titanium, stainless steel, and the like. Acetylene black may also be included in the cathode.

In preferred embodiments the electrodes are formed by mixing a polymeric binder with the anode and cathode materials in an appropriate liquid medium such as an organic  
10 solvent. This forms a paste or slurry, which is then coated onto a current collector grid, foil or mesh. The resulting intermediates are then pressed into a sheet form, dried and cut to appropriate dimensions.

To avoid electrical short circuits, a separator or a polymer electrolyte is also optionally disposed between the anode and cathode. Separators may comprise any suitable  
15 material such as a non-woven cloth of synthetic resin such as polytetrafluoroethylene, polypropylene, or polyethylene, or a woven porous body of such materials, polymer electrolytes and ceramic filled polymer electrolytes, or combinations of multi-layer composites.

## 20 Conductivity

Conductivity is especially important in solid and gel electrolyte batteries. For many years, solid and gel electrolytes having conductivities higher than  $10^{-3}$  S/cm were unknown at normal operating temperatures. US Patent 5,731,104 issued to Narang et al. (March  
1998) and related patents disclosed classes of liquid electrolyte plastics and plasticizers that  
25 permitted solid and gel electrolytes having  $10^{-3}$  S/cm.

In addition to having enhanced ambient temperature conductivity, the liquid electrolyte plasticizers can serve as plasticizers of polymer electrolytes and thereby adjust the mechanical properties of the polymer electrolytes. Polymer electrolytes/plasticizers formulations may be prepared to contain about 5 wt.% to 95 wt.% polymer, preferably about

10 wt. % to 50 wt. %, most preferably about 10 wt. % to about 25 wt. %, and may be solid, semi-solid, or liquid in phase.

The types of polymer electrolytes which can have their conductivity increased, often by as much as three orders of magnitude, include: 1) those which carry a negative charge and have a positively charged ionic species associated with them; 2) those which carry a positive charge and have a negatively charged ionic species associated with them; 3) those which are solid solutions having ionic species dissolved therein; and 4) those which are covalently functionalized with a moiety carrying an ionic species.

Examples of polymers useful as solid polymer electrolytes for purposes of the present invention include polyethers, polyesters, polyethylene oxides, oly(ethylene)imine, polyphosphazenes, polysiloxane, partially fluorinated polymethacrylates, or such polymers modified to include functionalized chains, e.g., alkylsulfonates, or the like. Such polymers can be synthesized by methods well known in the art or can be obtained commercially. The polymer backbone may also include copolymers of two or more polymers with repeating units of individual monomers.

Some examples of solid polymer electrolytes which carry a negative charge and have a positively charged ionic species associated with them are described in U.S. Patent No. 5,102,751 to Narang et al. (April 1992), incorporated by reference above. Examples of solid polymer electrolytes which are covalently functionalized with a moiety carrying an ionic species include those described in US Patent 5,548,055 issued to Narang et al. (August 1996), also incorporated by reference above.

Mechanically strong electrolyte films which have conductivities higher than  $10^{-3}$  S/cm may be formed from a combination of a liquid electrolyte plasticizer as disclosed and claimed herein or mixtures of such plasticizers, a strengthening material such as PVdF, a salt of the formula C-A, and, optionally, a solid polymer electrolyte and/or a high dielectric constant solvent such as propylene carbonate ("PC"), ethylene carbonate ("EC"), dimethoxyethane ("DME"), methoxyethoxy ethyl ether ("MEE"), and the like (see Table III). Preferably C-A is a lithium salt and the solid polymer electrolyte is a single-ion conductor polymer electrolyte as disclosed in US Patent 5,548,055 issued to Narang et al. (August 1996), incorporated by reference above. It may be necessary to add a glyme (e.g.,

dimethoxyethane ( $C_4H_{10}O_2$ ), diglyme ( $C_6H_{14}O_3$ ), triglyme ( $C_8H_{18}O_4$ ), tetraglyme ( $C_{10}H_{22}O_5$ ) or so on) to form a homogeneous blend of the SPE with PVdF; such compounds will typically serve not only as solvents but as additional plasticizing agents as well.

A preferred method of manufacturing conductive compositions containing liquid electrolyte plasticizers is a hot-press technique for forming films. Such a method typically involves: (1) forming a gel electrolyte composition by combining (I) a single-ion conducting SPE (e.g., a polysiloxane of Formula (I) or a copolymer containing mer units (II) and (III)), with (ii) an effective amount of liquid electrolyte plasticizer according to the invention for enhancing the ionic conductivity of that SPE and (iii) an amount of PVdF or an alternative material effective to enhance the mechanical strength of the composition; (b) heating the resulting combination at a temperature and for a time effective to form a fluid solution; (c) pressing the fluid solution; (d) cooling the solution; and (3) releasing the film so provided.

If waxes or gels are preferred, rather than films, the relative quantities of components can be adjusted to provide these alternative forms of conductive compositions. Compositions containing less electrolyte will generally form a gel, compositions containing slightly more electrolyte will generally form a wax, and compositions containing even more electrolyte will form a film. Alternative methods of manufacturing such conductive compositions will be readily apparent to those skilled in the art, or may be deduced from the relevant literature.

One should be able to take above-mentioned patents and the present concept of high densities of negatively charged substituents and construct large classes of electrolytes with this preferred conductivity of  $10^{-3}$  S/cm.

#### **Formation of the Solid Electrolyte Interface**

Addition of **Structure I** to the original electrolyte can result in the formation of an enhanced solid electrolyte interface (SEI) between the anode and the electrolyte.

Metal ion batteries are usually constructed by separately forming an anode and a cathode, placing an electrolyte between the anode and cathode to form a battery, and then giving the battery an initial charge. Components in the electrolytes used in known metal-ion

batteries are sometimes thermodynamically unstable at the electrode potentials employed, and the initial charging of such batteries results in breakdown of such components at the anode and sometimes also at the cathode. This causes the so-called "first cycle capacity loss" or "irreversible capacity loss". The electrolyte breakdown attending the initial  
5 charging cycle occurs significantly at first, but is greatly reduced by the formation of a passivating surface film on the electrode. This passivating surface film is known in the industry as a solid electrolyte interface (SEI).

Substantially compatible electrolytes with respect to a particular anode material are those which tend to form an effective SEI on that material, while substantially incompatible  
10 electrolytes are those which generally fail to form an effective SEI on the anode material and undergo decomposition on the electrode. Where an electrolyte composition contains many electrolyte species, including perhaps multiple solvents, the electrolyte composition is taken as a whole when determining whether or not the electrolyte composition is substantially compatible or substantially incompatible. There are, of course, boundary conditions in  
15 which an electrolyte forms an effective SEI with a given anode material either very slowly, or only under special conditions. In such boundary conditions the electrolyte is deemed to be substantially incompatible with the anode material. It should also be understood that the terms "compatible" and "incompatible" are specific to particular anode materials. Propylene carbonate, for example, is substantially compatible with coke anodes, but substantially  
20 incompatible with graphite anodes.

Timely formation of a solid electrolyte interface reduces the first cycle capacity loss. In commercially available metal ion batteries, for example, first cycle capacity loss is generally limited to less than about 5-10%. In addition, an effective SEI is substantially impermeable to electrolyte, while still being relatively permeable to metal ions. This  
25 provides metal ion battery electrolytes with kinetic stability, and results in good cycle life.

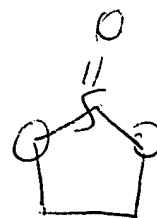
The following examples are intended to provide those of ordinary skill in the art with a complete disclosure and description of how to make and use the novel electrolyte compositions of the invention, and are not intended to limit the scope of what the inventors regard as their invention in any way. Efforts have been made to ensure accuracy with  
30 respect to numbers used (e.g., amounts, temperatures, etc.), but some experimental error and

deviation should, of course, be allowed for. Unless otherwise indicated, parts are parts by weight, temperatures are in degrees centigrade, and pressure is at or near atmospheric. All chemicals, reagents, and the like, are commercially available or are otherwise readily synthesized using conventional techniques well known in the art.

5

**Example 1 - Preparation of Lithium Ion Battery Containing Ethylene Sulfite as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 1 % wt of ethylene sulfite. The solution was added to a lithium ion cell consisting of a graphite electrode, a separator, and a lithium cobalt oxide cathode.



**Example 2 - Preparation of Lithium Ion Battery Containing Butadiene Sulfone as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 2 % wt of butadiene sulfone. The solution was added to a lithium ion cell consisting of a graphite electrode, a separator, and a lithium cobalt oxide cathode.

**Example 3 - Preparation of Lithium Ion Battery Containing Sulfur Trioxide Pyridine as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 2 % wt of sulfur trioxide pyridine complex. The solution was added to a lithium ion cell consisting of a graphite electrode, a separator, and a  $\text{LiMn}_2\text{O}_4$  cathode.

**Example 4 - Preparation of Lithium Ion Battery Containing Isobutylnitrate as an Electrolyte Additive**

25

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 2 % wt of isobutylnitrate. The solution was added to a lithium ion cell consisting of a graphite electrode, a separator, and a lithium cobalt oxide cathode.

**Example 5 - Preparation of Lithium Ion Battery Containing Isopropylnitrite as an Electrolyte Additive**

In the battery of Example 4, the electrolyte additive may be replaced by isopropylnitrite.

5      **Example 6 - Preparation of a Lithium Ion Battery Containing Sulfur Trioxide Pyridine as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:2 by weight) and 2 % wt of sulfur trioxide pyridine complex. The solution was added to a lithium cell  
10      consisting of a lithium metal electrode, a separator, and a lithium cobalt oxide cathode.

**Example 7 - Preparation of a Lithium Ion Battery Containing Ethylene Trithiocarbonate as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and  
15      1 % wt of ethylene trithiocarbonate. The solution was added to a lithium cell consisting of a lithium metal electrode, a separator, and a  $\text{LiMn}_2\text{O}_4$  cathode.

**Example 7 - Preparation of a Lithium Ion Battery Containing Azoxymethane as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system  
20      composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 0.5 % wt of azoxymethane. The solution was added to a lithium cell consisting of a lithium metal electrode, a separator, and a lithium cobalt oxide cathode.

**Example 8 - Preparation of Polymer Electrolyte Film Containing Butadiene Sulfone.**

25      In a dry box, lithium hexafluorophosphate (1 g.), polyvinylidene fluoride (2g.), and a composition of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 1 % wt of butadiene sulfone were mixed and heated to 120°C until a clear melt was obtained. The hot melt was poured into a mold and hot pressed. Upon cooling to room  
30      temperature, a free-standing film was obtained.

**Example 9 - Preparation of Polymer Electrolyte Film Containing Isobutylnitrate.**

In a dry box, lithium hexafluorophosphate (1 g.), polyvinylidene fluoride (2g.), and a composition of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 1.5 % wt of isobutylnitrate were mixed and heated to 120°C until a clear melt was obtained. The hot melt was poured into a mold and hot pressed. Upon cooling to room temperature, a free-standing film was obtained.

**Example 10 - Preparation of Lithium Ion Battery Containing Sulfur Trioxide Pyridine as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate (1:1 by weight) and 2 % wt of sulfur trioxide pyridine complex. The solution was added to a lithium ion cell consisting of a graphite electrode, a separator, and a  $\text{LiMn}_2\text{O}_4$  cathode.

**Example 11- Preparation of a Lithium Ion Battery Containing Ethylene Trithiocarbonate as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate (1:1 by weight) and 1 % wt of ethylene trithiocarbonate. The solution was added to a lithium cell consisting of lithium metal electrode, separator, and  $\text{LiMn}_2\text{O}_4$  cathode.

**Example 12 - Preparation of Lithium Primary Battery Containing Butadiene Sulfone as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system consisting of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 1 % wt of butadiene sulfone. The solution was added to a lithium cell consisting of a lithium metal anode, a separator, and a  $\text{FeS}_2$  cathode.

**Example 13 - Preparation of a Primary Lithium Battery Containing Isobutylnitrate as an Electrolyte Additive**

A solution of lithium hexafluorophosphate was prepared in a solvent system consisting of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and

2 % wt of isobutylnitrate. The solution was added to a lithium ion cell consisting of a lithium metal anode, a separator, and manganese dioxide cathode.

**Example 14 - Preparation of a Lithium Ion Battery Containing Azobis(isobutyronitrile) (AIBN) as an Electrolyte Additive**

5        A solution of lithium hexafluorophosphate was prepared in a solvent system composed of ethylene carbonate/dimethylcarbonate/triethylphosphate (1:1:1 by weight) and 1 % wt of azobis(isobutyronitrile) (AIBN). The solution was added to a lithium cell consisting of a lithium metal electrode, a separator, and a lithium cobalt oxide cathode.

10       It is contemplated that batteries with an improved electrolyte as described herein will be employed in all manner of portable electronics including computers, cell phones and other portable phones, as well as larger applications such as battery backup systems, and electric and hybrid motor vehicles.

15       All other aspects of contemplated batteries and battery fabrication methods may be entirely conventional, and any details not specifically related herein are available in the literature. Thus, the size, shape and configuration of contemplated batteries are not particularly critical. In many instances, for example, batteries according to the present invention will have only a single cell, but more commonly such batteries will have multiple cells. Similarly, individual cells may be fabricated into any suitable shape, including flat cells and jelly roll configurations.

20       Thus, specific embodiments and applications of gas generating electrolyte additives have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. For example, electrolytic compositions disclosed herein can be used in capacitors, in surface treatment of metals, in situations where non-oxidizing/inert environments are required, for building over pressure in sealed containers, for storage of materials needing a gas blanket, preferably flammable materials, and as gas propellants in drug delivery. The inventive subject matter, therefore, is not to be restricted except in the spirit of the appended claims.

Table 2

Number	Compound
1	
2	
3	
4	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{O}-\overset{\oplus}{\text{N}}=\overset{\text{O}}{\text{O}}^-$
5	$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{CH}-\text{O}-\text{N}=\text{O} \\ \diagup \\ \text{H}_3\text{C} \end{array}$
6	
7	$\text{H}_3\text{C}-\overset{\oplus}{\text{N}}=\text{N}-\text{CH}_3$

Table 2 (continued)

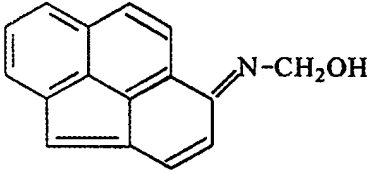
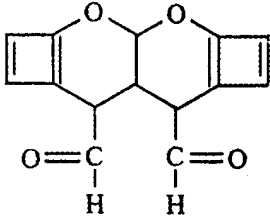
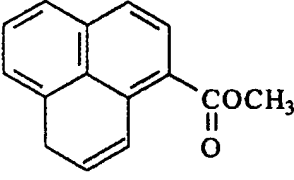
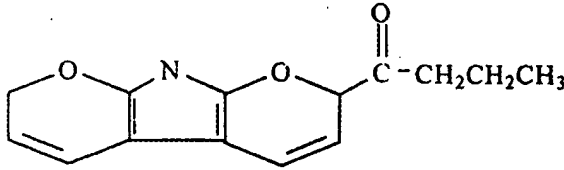
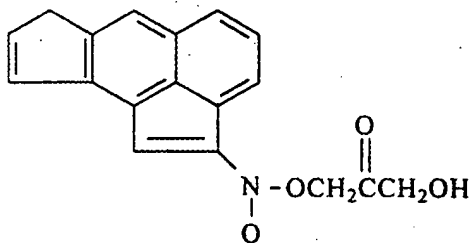
Number	Compound
8	$  \begin{array}{c}  \text{H}_3\text{C} \quad \quad \text{CH}_3 \\    \quad \quad   \\  \text{H}_3\text{C}-\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_3 \\    \quad \quad   \\  \text{CN} \quad \quad \text{CN}  \end{array}  $
9	$\text{Fe}(\text{CO})_5$
10	$  \text{H}_3\text{CCH}_2\text{CH}_2\text{N}=\text{NCH}_2\text{CH}_2\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{CH}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{CH}_2\text{CH}_3  $
11	
12	
13	
14	

Table 2 (continued)

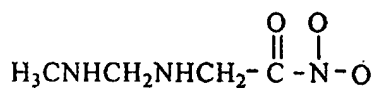
Number

Compound

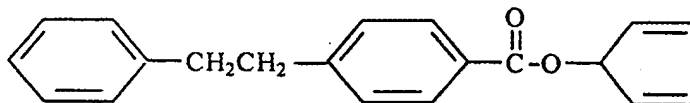
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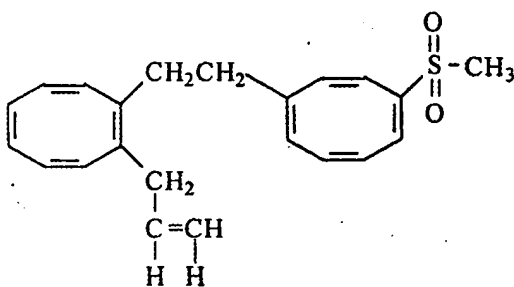
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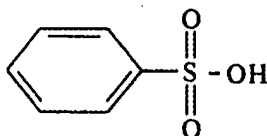
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18



19



20

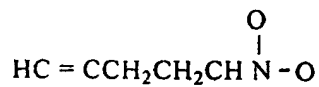


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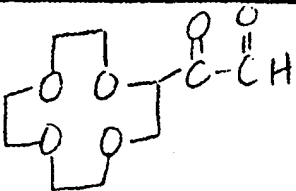
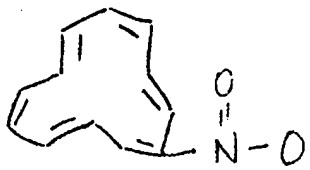
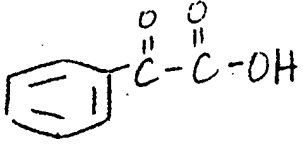
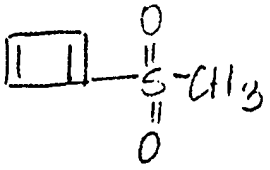
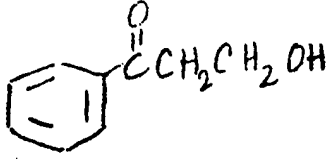
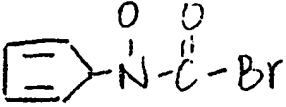
Number	Compound
21	
22	$\text{HC}\equiv\text{CCH}=\text{CHCH}(\text{N}=\text{O})\text{O}$
23	
24	
25	
26	
27	

Table 2 (continued)

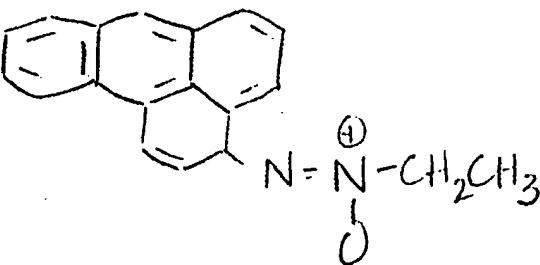
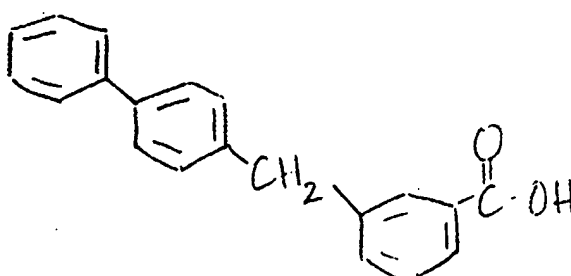
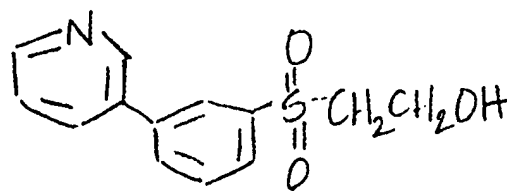
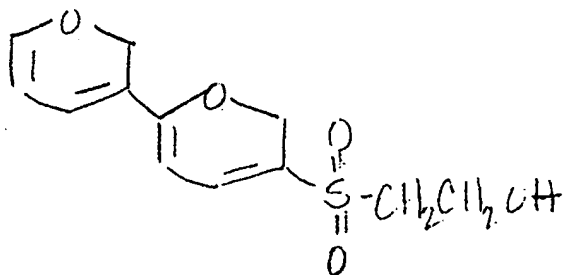
Number	Compound
28	$\text{HO}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{CH}_2\overset{\text{H}}{\underset{ }{\text{C}}}=\overset{\text{H}}{\underset{ }{\text{C}}}-\text{N}=\text{N}-\text{H}$
29	$\text{H}_3\text{CCH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}$
30	
31	
32	

Table 2 (continued)

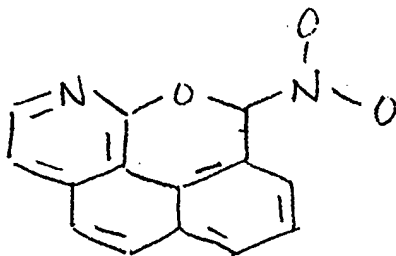
Number

Compound

33



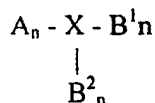
34



## CLAIMS

We claim:

1. An improved battery having an electrolyte and at least two electrodes, the improvement comprising a compound that generates a fire-retardant gas upon decomposition, whereby the compound has the formula:



wherein,

X = N, C, S, NO, N<sub>2</sub>, CO, SO;

A = aryl (including conjugated, non-conjugated), alkyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkenyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkoxy (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), aralkylene (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), annulene (i.e. completely conjugated monocyclic polyenes), conjugated hydrocarbons (such as fulvene, calicene, fulvalene, methylenecyclopropene), fused ring systems (such as naphthalene, anthracene, naphthacene, phenanthrene, triphenylene, pyrene, perylene, butalene, pentalene, azulene, heptalene, biphenylene, acenaphthylene), heteroatoms (including halogen, alkali metals, transition metals), alcohol (such as phenol, ethanol, butanol), hydroxyl, acetal, or ketal;

B<sup>1</sup> and B<sup>2</sup> = null, oxygen, hydrogen, aryl (including conjugated, non-conjugated), alkyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkenyl (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), alkoxy (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), aralkylene (including branched, straight-chain, conjugated, non-conjugated, heteroatom substituted), annulene (i.e. completely conjugated monocyclic polyenes), conjugated hydrocarbons (such as fulvene, calicene, fulvalene, methylenecyclopropene), fused ring systems (such as naphthalene, anthracene, naphthacene, phenanthrene, triphenylene, pyrene, perylene, butalene, pentalene, azulene, heptalene, biphenylene, acenaphthylene), heteroatoms (including halogen, alkali metals, transition metals), alcohol (such as phenol, ethanol, butanol),

hydroxyl, acetal, or ketal;

n = an integer from 0-100;

where B<sup>1</sup> and B<sup>2</sup> are not null simultaneously;

where B<sup>2</sup> is null when X is N<sub>2</sub>; and

where B<sup>1</sup> and B<sup>2</sup> are not oxygen when X is CO.

2. The battery of claim 1 wherein the electrolyte is chemically or electrochemically unstable on the electrode.
3. The battery of claim 1 wherein the electrolyte is chemically or electrochemically stable on the electrode.
4. The battery of claim 1 wherein at least one of the electrodes comprises at least one of lithium, lithium or other alloy, carbon, metal-oxide, metal sulfide and an intercalation material.
5. The battery of claim 1 wherein the electrolyte comprises a solid polymer.
6. The battery of claim 1 wherein at least one of the electrodes comprises lithium and the electrolyte comprises a solid polymer.
7. The battery of claim 1 wherein the battery has a conductivity greater than 10<sup>-3</sup> S/cm.
8. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula CO.
9. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula SO<sub>2</sub>.
10. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula SO<sub>3</sub>.
11. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula NO.
12. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula N<sub>2</sub>O.
13. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula NO<sub>2</sub>.
14. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula N<sub>2</sub>.
15. The battery of any of claims 1-7 wherein the gas assists in formation of a solid electrolyte interface (SEI) between the electrolyte and at least one of the electrodes.

16. The battery of any of claims 1 - 7 wherein the compound comprises a nitrite.
17. The battery of any of claims 1 - 7 wherein the compound comprises a sulfate.
18. The battery of any of claims 1 - 7 wherein the compound comprises a sulfite.
19. The battery of any of claims 1 - 7 wherein the compound comprises a sulfone.
20. The battery of any of claims 1 - 7 wherein the compound includes an azo component.
21. The battery of any of claims 1 - 7 wherein the compound includes an azoxy component.

**AMENDED CLAIMS**

[received by the International Bureau on 10 May 1999 (10 05.99);  
original claim 1 amended; remaining claims unchanged (2 pages)]

hydroxyl, acetal, or ketal;

$n$  = an integer from 0-100;

where  $B^1$  and  $B^2$  are not null simultaneously;

where either  $B^1$  or  $B^2$  are null when  $X = N$ ;

where  $A$ ,  $B^1$ , or  $B^2$  are not chalcogen when  $X = C$ ;

where  $B^2$  is null when  $X$  is  $N_2$ ; and

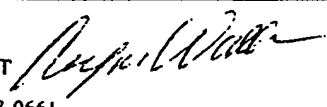
where  $B^1$  and  $B^2$  are not oxygen when  $X$  is  $CO$ .

2. The battery of claim 1 wherein the electrolyte is chemically or electrochemically unstable on the electrode.
3. The battery of claim 1 wherein the electrolyte is chemically or electrochemically stable on the electrode.
4. The battery of claim 1 wherein at least one of the electrodes comprises at least one of lithium, lithium or other alloy, carbon, metal-oxide, metal sulfide and an intercalation material.
5. The battery of claim 1 wherein the electrolyte comprises a solid polymer.
6. The battery of claim 1 wherein at least one of the electrodes comprises lithium and the electrolyte comprises a solid polymer.
7. The battery of claim 1 wherein the battery has a conductivity greater than  $10^{-3}$  S/cm.
8. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula  $CO$ .
9. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula  $SO_2$ .
10. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula  $SO_3$ .
11. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula  $NO$ .
12. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula  $N_2O$ .
13. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula  $NO_2$ .

14. The battery of any of claims 1 - 7 wherein the gas comprises a molecule having the formula  $N_2$ .
15. The battery of any of claims 1-7 wherein the gas assists in formation of a solid electrolyte interface (SEI) between the electrolyte and at least one of the electrodes.
16. The battery of any of claims 1 - 7 wherein the compound comprises a nitrite.
17. The battery of any of claims 1 - 7 wherein the compound comprises a sulfate.
18. The battery of any of claims 1 - 7 wherein the compound comprises a sulfite.
19. The battery of any of claims 1 - 7 wherein the compound comprises a sulfone.
20. The battery of any of claims 1 - 7 wherein the compound includes an azo component.
21. The battery of any of claims 1 - 7 wherein the compound includes an azoxy component.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/25466

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) :H01M 10/40 US CL :429/307, 347 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 429/307, 347, FOR108 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,102,751 A (NARANG et al) 07 April 1992 (07-04-92), column 2, lines 57-63, column 7, lines 30-35.	1, 2, 4-8, 11-14
X	US 4,851,307 A (ARMAND et al) 25 July 1989 (25-07-89), column 1, line 65-column 2, line 15, column 4, lines 29-37.	1, 2, 4-7, 9, 11-14, 19
X	US 4,452,868 A (GIBBARD et al) 05 June 1984 (05-06-84), column 6, lines 10-22.	1, 3, 8, 11-14
X	US 3,775,183 A (PAULSON) 27 November 1973 (27-11-73), column 1, lines 61-67, column 3, lines 3-17.	1, 3, 11-14
X	US 4,801,511 A (YOUNG) 31 January 1989 (31-01-89), column 4, lines 45-64.	1, 3, 8
X	JP 61-2278 A (OOMORI) 08 January 1986, abstract, lines 7-10.	1, 3, 11-14
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family	
Date of the actual completion of the international search 10 FEBRUARY 1999		Date of mailing of the international search report 09 MAR 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer STEPHEN J. KALAFUT  Telephone No. (703) 308-0661